

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Fungicidal Concentrates

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organized under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a liquid concentrate formulation for fungicidal mixtures.

Frequently, it is advantageous to apply fungicidal compositions containing two previously known fungicides in combination and this is true with respect to 2-heptadecylglyoxalidine (hereinafter referred to as "glyoxalidine") and *n*-dodecylguanidine acetate (hereinafter referred to as "guanidine").

The utility of this fungicidal mixture has, however, been limited by the solubility characteristics of the two components which are such as to have heretofore precluded development of a stable liquid formulation concentrate. Such a concentrate is convenient to use and thus preferred by orchardists. The glyoxalidine is a waxy solid with a melting point of 62° C. to 68° C. and is thus not readily formulated as a wettable powder. Commercially, it is sold in an isopropanol solution containing 30 per cent by weight of 2-heptadecylglyoxalidine in the form of its acetate salt. The guanidine is normally available as a wettable powder formulation containing 65 per cent by weight of *n*-dodecylguanidine acetate, the remainder being an inert particulate solid carrier, e.g., bentonite, and about 5 per cent of a surfactant.

One known aqueous formulation of the fungicidal mixture is a liquid mix in which a 30 per cent solution of the "glyoxalidine" in isopropanol and the "guanidine" as a 65 per cent wettable powder are charged into a tank full of water and the resulting mixture is continuously agitated to keep the components in suspension. In the other formulation a dry

product is applied as a spray by suspending the dry powder in a large volume of water and maintaining vigorous agitation.

The difficulty with these known formulations is that they require handling of a dust material by the applicator which involves mixing problems, contamination of persons and facilities, and waste of some material. In addition, the tank water needs to be continuously agitated to maintain suspension of the dust.

The present invention provides a liquid concentrate in which the technical "glyoxalidine" and "guanidine" have been mixed in proportions optimum for fungicidal effectiveness. The invention utilizes the technically pure active fungicidal ingredients and thus obviates prior formulation of the "glyoxalidine" in isopropanol and of the "guanidine" as a wettable powder as required by the prior art techniques. Being a liquid concentrate, the present formulation is easy to handle and obviates all the problems of working with a dust described above. In addition, the liquid concentrate of this invention forms a solution when added to water so that the actual spray need not be kept under constant agitation.

Essentially, the present invention comprises liquid concentrate formulations containing "glyoxalidine" and "guanidine" characterized by the presence of propylene glycol. It has been found that when certain percentages of propylene glycol are added to the two-component fungicidal mixture, a stable liquid concentrate formulation is obtained which exhibits excellent sprayability when mixed with water. In this respect the use of propylene glycol has been found critical inasmuch as the use of other common solvents did not result in usable formulations but rather led to formation of turbid suspensions not suited for mixing or spraying.

The compositions of this invention may contain the two active fungicidal components in a proportion of from 0.8 part by weight to 15 parts by weight of "glyoxalidine" per part

- by weight of "guanidine". However, in preferred combinations, from 1 to 8 parts of "glyoxalidine" are provided for every part of "guanidine" and the optimum ratio is 4 parts of "glyoxalidine" for every part of "guanidine". Use of this ratio appears to result in most effective disease control. The compositions are further characterized in that they contain from 10 to 30 parts by weight of propylene glycol per part by weight of "guanidine". It has been found that at least 10 parts by weight of propylene glycol per part of "guanidine" are required to give readily water-dilutable concentrates. Use of more than 30 parts of propylene glycol results in low toxicity concentration in the concentrate and gives no advantages in stability or sprayability of the diluted concentrate. In addition, the compositions may contain a certain amount of isopropanol or other solvent in which the technical "glyoxalidine" material may be commercially available. The liquid concentrate formulations of this invention thus contain from 10 to 40 per cent by weight of 2-heptadecylglyoxalidine, from 3 to 10 per cent by weight of n-dodecylguanidine acetate, and from 50 to 87 per cent by weight of propylene glycol, provided that at least 10 parts by weight of propylene glycol are provided for every part by weight of n-dodecylguanidine acetate.
- The liquid concentrates are prepared by physically admixing the components in the above-indicated ratios to result in a clear solution. If the concentrates are used at very low temperatures (ca. 0° C.) slight warming may be necessary to maintain a clear, readily dilutable concentrate. If one of the fungicidal components is available in solution, e.g., "glyoxalidine" in isopropanol, such a solution may be admixed with the other components of the concentrate and the isopropanol optionally evaporated by distillation under reduced pressure.
- To demonstrate the criticality of using propylene glycol comparative tests were carried out using the following materials in place of propylene glycol:
- ethylene glycol,
 - isopropanol,
 - monobutyl ether of ethylene glycol,
 - dimethylformamide,
 - dimethylsulfoxide,
 - monoethyl ether of diethylene glycol monoacetate,
 - monomethyl ether of ethylene glycol acetate,
 - ethylene glycol diacetate,
 - 1,5-butanediol,
 - glycerol.
- Use of each of the above materials in the amounts indicated for propylene glycol results in a cloudy, turbid suspension unsuitable for agricultural application.
- To determine the effectiveness of the formulation of this invention in agricultural applications, the formulation of this invention was applied to combat bean mildew, bean rust, tomato early blight and cucumber anthracnose in side-by-side tests with the conventional formulations described above, according to the following procedure.
- Bean, tomato, and cucumber plants were sprayed on a revolving turntable with the indicated formulation for 30 seconds to apply about 100 milliliters of formulation. The treated plants were then stored at room temperature for a period of 24 hours. After the storage period, one half of the plants were sprayed on the turntable with 200 millilitres of water (indicated as rain treatment) and then dried. The remaining half received no additional treatment. Then all of the test plants were infested with the indicated fungus by brushing their leaves lightly with infested plants from a stock culture, or by spraying them with a stock spore suspension. The plants were held for seven to ten days at conditions optimum for fungal growth. The degree of protection on primary leaves was visually rated according to the following designations:
- 1=no activity
 - 2=little control
 - 3=about 50% effective
 - 4=excellent control
 - 5=complete control
- The results are set forth in Table I, below. Concentrations of the active toxicants in the applied formulation are given in parts per million for each toxicant.

TABLE I
Fungicidal Test Results for Combinations of "Glyoxalidine" and "Guanidine" in Different Formulations

Formulation	Concentration of active toxicant in water (ppm)	Ratings				Counts ²			
		Early Blight		Bean Rust		Cucumber	Anthraco- nose		
		No Rain	Rain ³	No Rain	Rain ³	No Rain	Rain ³		
"Guanidine" (technical) ¹	250	3	3	4	3	4	5	9	23
	60	4	4	3	3	4	4	39	89
	15	2	2	2	2	3	3	56	84
"Guanidine" (65% wettable powder)	250	2	2	3	3	4	4	5	28
	60	2	3	4	4	4	4	63	49
	15	3	3	2	2	3	3	78	dead
"Glyoxalidine" (30% solution in isopropanol)	1035	2	2	2	2	5	5	70	28
	259	2	2	2	2	4	4	44	57
	65	1	1	1	1	1	4	64	42
"Glyoxalidine" (30% solution in isopropanol + "Guanidine" (technical)	1035 + 250	*	*	*	*	5	5	31	—
	259 + 60	3	3	3	3	5	5	22	56
	65 + 15	3,	3	3	3	5	4	32	36
"Glyoxalidine" (30% solution in isopropanol) + "Guanidine" (65% wettable powder)	1035 + 250	*	*	*	*	5	5	26	—
	259 + 60	4	4	4	4	5	4	53	40
	65 + 15	4	4	3	3	5	5	66	65
"Glyoxalidine" (technical) + "Guanidine" (technical) in propylene glycol ⁴	1035 + 250	*	*	*	*	5	5	34	36
	259 + 60	4	4	4	4	5	4	39	59
	65 + 15	3	3	4	4	3	4	48	43
Control	—	1	1	1	1	1	1	136	169

1. Dissolved in ethyl alcohol before addition of water. The final formulations at 250 ppm contained 10 per cent alcohol by volume.

2. Number of lesions per 4 leaves.

3. Water (200 ml.) sprayed on plants 24 hours after treatment.

4. The concentrate contained 65 per cent by weight of propylene glycol in each instance.

* The sprayed plants showed a phytotoxic response.

It can be seen that the liquid formulation of this invention possesses the advantages of a liquid formulation with undiminished fungicidal effectiveness.

- 5 According to one embodiment of the present invention there is provided a fungicidal liquid concentrate formulation comprising from 25 to 28 percent by weight of 2-heptadecylglyoxalidine, from 6 to 8 per cent by weight of
10 n-dodecylguanidine acetate and 65 per cent by weight of propylene glycol.

WHAT WE CLAIM IS:—

1. A fungicidal liquid concentrate formulation comprising from 10 to 40 per cent by
15 weight of 2-heptadecylglyoxalidine, from 3 to 10 per cent by weight of n-dodecylguanidine acetate, and from 50 to 87 per cent by weight of propylene glycol, there being at least 10 parts by weight of propylene glycol per part
20 by weight of n-dodecylguanidine acetate.

2. A fungicidal concentrate as claimed in claim 1 in which there are 10 to 30 parts by weight of propylene glycol per part by weight of n-dodecylguanidine acetate.

- 25 3. A fungicidal concentrate as claimed in claim 2 in which there are 10 parts by weight of propylene glycol for every part of n-dodecylguanidine acetate.

4. A fungicidal concentrate as claimed in any of claims 1 to 3 in which there are 0.8 to
30 15 parts by weight of 2-heptadecylglyoxalidine per part by weight of n-dodecylguanidine acetate.

5. A fungicidal concentrate as claimed in claim 4 in which there are 1 to 8 parts by
35 weight of 2-heptadecylglyoxalidine per part by weight of n-dodecylguanidine.

6. A fungicidal concentrate as claimed in claim 5 in which there are 4 parts by
40 weight of 2-heptadecylglyoxalidine per part by weight of n-dodecylguanidine.

7. A fungicidal concentrate as claimed in claim 1 comprising from 25 to 28 per cent
45 by weight of 2-heptadecylglyoxalidine, from 6 to 8 per cent by weight of n-dodecylguanidine acetate, and 65 per cent by weight of propylene glycol.

8. A fungicidal concentrate according to claim 1 substantially as hereinbefore
50 described.

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